(54) Title: METHOD FOR THE PREPARATION OF AN OLEFIN POLYMERIZATION CATALYST CONSISTING OF PARTICLES OF EQUAL SIZE

(57) Abstract

In the invention a particular procatalyst composition intended for the polymerization of olefins is prepared by reacting the carrier particles consisting of a $MgCl_2$-C_2H_5OH-complex with $TiCl_4$. When the method is applied into pilot-scale it was noticed that the procatalyst composition obtained produced olefin polymer, the finely-divided material portion of which was deterioratingly high. This was caused by the fact that the procatalyst composition particles had decomposed to finely-divided material during the synthesis, which was then in the polymerization repeated in the polymer structure due to the so-called replica phenomenon. In the invention it has unexpectedly been noticed that the breaking of the carrier particles is not a result of e.g. mechanical strain but of the fact that when the carrier particles react with the $TiCl_4$ a heavy discharge of hydrogen chloride is first occurring as a result of the reaction which breaks the carrier particles. The carrier particles can, according to the invention, be maintained undamaged during the reaction by distributing the release in the reaction or from the reaction of the hydrogen chloride created in the reaction to a molar velocity not exceeding the fivefold value of the molar mean velocity of the release. This is achieved among other things by adding reagents unusually slowly, by using lower temperatures and heating velocities, by intensifying the agitation, by using an overpressure and/or by conducting diluting inert gas into the reaction mixture.

Method for the preparation of an olefin polymerization
catalyst consisting of particles of equal size

5   The invention relates to a method for the preparation of a
       particulate procatalyst composition intended for the poly-
       merization of olefins by reacting the carrier particles
       consisting of a $MgCl_2$-C_2H_5OH-complex with $TiCl_4$.

10   For the polymerization of olefins, generally, the Ziegler-
       Natta-catalyst system, which consists of a so-called pro-
       catalyst and a co-catalyst, is used. The procatalyst is
       based on a compound of a transition metal belonging to any
       of the groups IVA-VIII (Hubbard) of the periodical table
15   of the elements and the co-catalyst is based on an or-
       ganometallic compound of a metal belonging to any of the
       groups IA-III(A) (Hubbard) of the periodical table of the
       elements. The catalyst system can also comprise a carrier,
       on which the transition metal compound is layered, and
20   electron donor compounds improving and modifying the cata-
       lytic properties.

       When Ziegler-Natta-procatalysts intended for the polymeri-
       zation of olefins and particularly of propene are prepa-
25   red, carrier particles consisting of solid magnesium chlo-
       ride and ethanol are reacted with titanium tetrachloride.
       As a result a magnesium chloride is created, the crystal
       structure of which is strongly modified, i.e. becoming in
       practice amorphous and which can coordinate with titanium
30   tetrachloride. Thus, the titanium tetrachloride, which has
       been combined with the amorphous magnesium chloride, then
       forms the active centers of the catalyst. As byproducts of
       this process hydrogen chloride and ethoxy titanium tri-
       chloride (1, 2) are formed:

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       $$MgCl_2.EtOH + TiCl_4 = MgCl_2.+ TiCl_3.OEt + HCl \qquad (1)$$
       $$10MgCl_2. + TiCl_4 = 10MgCl.TiCl_4 \qquad\qquad (2)$$
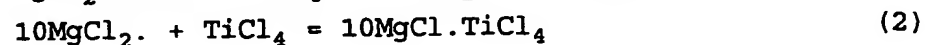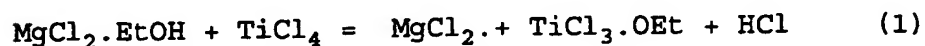
       In laboratory conditions polyolefins have been obtained
40   using the procatalysts prepared in this manner. The acti-

vity of the catalyst has been good. The particle size, particle size distribution and other properties of the polyolefins have been satisfactory.

When going over from laboratory scale to production in larger scale it has, however, been noticed that the particle size distribution of the polymer product is everything but satisfactory. The product contains, namely, compared with a product prepared with a laboratory procatalyst very great amounts of finely-divided substance or material, the diameter of which is less than 1mm. This can be seen among other things in fig. 1, where the portion of the finely-divided material becomes multiplied when going over from a laboratory-prepared procatalyst to a procatalyst prepared in pilot-scale. A so-called "replica"-phenomenon prevails in polymerization using this kind of a procatalyst. This means that the morphology of the polymer particles created corresponds to the morphology of the procatalyst used in the preparation of the polymer, it could right off be assumed that the creation of the finely-divided material in the polymer was a result of the decomposition of the procatalyst particles intended for the polymerization in connection with the pilot-scale preparation.

In the preparation of the procatalysts it was unexpectedly noticed that there prevailed a clear correlation between the maximum value of the releasing velocity of the hydrogen chloride created in the reaction (1) and the portion of the finely-divided substance. This correlation is presented in fig. 2. The figure shows that the portion of the finely-divided polymer increases when the momentary hydrogen chloride discharge strengthens. In the same connection it was noticed that the hydrogen chloride discharge strengthened when the ethanol portion of the magnesium chloride-ethanol complex increased. From this an idea came out that the scale-up problem of the catalyst preparation

attached with the creation of the finely-divided polymer
would result from a too heavy release of the hydrogen
chloride.

5   For this reason a system, in which there was present mag-
nesium chloride diethanol complex, titanium tetrachloride
and hydrogen chloride created in a reaction between these
components, a system, in which there was present only
titanium tetrachloride and hydrogen chloride, and a sys-
10 tem, in which there was present magnesium dichloride,
titanium tetrachloride and hydrogen chloride, were compa-
red with each other.

When the first-mentioned system was heated from the tempe-
15 rature -20°C to the temperature of +110°C a heavy dischar-
ge of hydrogen chloride took place between +10°C and
+20°C, after which the formation of the hydrogen chloride
became normalized corresponding to the normal behaviour of
a dissolved gas at the temperature of above 40°C. This
20 phenomenon can be seen in figures 3 and 4, figure 3 of
which presents the amount of the hydrogen chloride re-
leased from the system (expressed as the consumption of
NaOH) as a function of the temperature and the reaction
time and figure 4 presents the releasing velocity of hyd-
25 rogen chloride of the system as a function of the tempera-
ture.

In the second- and third-mentioned systems, of which mag-
nesium chloride ethanol complex was missing no discharge
30 of the above-mentioned type was observed.

On the basis of the preliminary tests it could thus be
noted that the creation of the detrimental finely-divided
polyolefin when a procatalyst prepared in pilot-scale was
35 used, which has been obtained from a reaction between the
$MgCl_2$-C_2H_5OH complex particles and $TiCl_4$, is essentially a
result thereof that the reaction mentioned and presented

in the reaction equation (1) produces on one time so much hydrogen chloride that when it is gasified at once it blows the carrier particles into finely-divided material, which then repeats in the polyolefin to be created.

5   The aim of the invention is to provide a method for the preparation of a particulate procatalyst composition inteded for the olefin polymerization. The procatalyst compo- sition should be created using a method giving a usable particle size distribution, from which the finely-divided

10   material is essentially missing. Moreover, the particles must be suitable for use as to their shape, chemical com- position, activity and stereospecifity. In this invention it is also tried to see to it that the polymer prepared by the procatalyst composition does not contain finely-divi-

15   ded material to any considerable amount. An aim is simul- taneously a polyolefin, the particle shape, isotacticity and crystallinity, melt viscosity and bulk density of which are suitable for use.

20   This aim taken has now been reached by a new method for the preparation of the particulate procatalyst intended for the polymerization of olefins, which is mainly charac- terized by what is mentioned in the characterizing clau-

25   se of claim 1. It has thus been realized that the carrier particles consisting of $MgCl_2-C_2H_5OH$-complex expressly de- compose as a result of a hydrogen chloride discharge, when they are activated with titanium tetrachloride. (Previously it was believed that the decomposition among

30   other things is a result of the mechanical strain caused by the mixing). This phenomenon occurs above all when the preparation of the procatalyst takes place in larger, e.g. in pilot-scale. Due to the decomposition of the carrier particles both the carrier and thus also the procatalyst

35   composition contains a great deal of finely-divided ma- terial. The particle size distribution of the procatalyst composition then repeats in the polymerization in the

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particle size distribution, whereby even the polymer comp-
rises a great deal of finely-divided material.

The above-mentioned realization that the great amount of
the finely-divided material in the polymer product is a
result of the heavy discharge of the hydrogen chloride gas
in the procatalyst synthesis, enables such a method for
the preparation of a procatalyst, which gives a procata-
lyst composition and also a polyolefin containing very
little finely-divided material. In the method the carrier
particles are maintained undamaged during the reaction by
distributing the release of the created hydrogen chloride
in the reaction or from the reaction mixture to a molar
velocity which does not exceed the fivefold molar mean
velocity value. When scanning again the figures 3 and 4 it
is noticed that without the special measures according to
the invention the maximal velocity of the discharge of the
hydrogen chloride rises to a value corresponding to a
NaOH-consumption of about 16ml/°C, the mean discharge
velocity being of an order corresponding to the NaOH-con-
sumption of about 2ml/°C. These valves corresponds to an
experimental arrangement where 0.1 mol of $MgCl_2.3EtOH$ is
reacted with 300 ml of $TiCl_4$. In the experiment concerned
the hydrogen chloride discharge of a system was measured,
the complex of which contained three ethanol molecules as
per one magnesium chloride molecule, whereby the discharge
peak of the hydrogen chloride thus was about eight times
as high as the mean discharge velocity. Be it mentioned
that when the complex contains 4.5 moles ethanol as per
magnesium chloride mole the maximal discharge corresponded
to even a NaOH-consumption of 90ml/°C, the mean volume
velocity of the hydrogen chloride release being cf the
order corresponding to a NaOH-consumption of 1-5ml/°C i.e.
the discharge was above 20-fold compared with the mean
value of the release velocity.

Figure 4 also shows that the release of the hydrogen
chloride should be restricted so that not more than about
5% could be discharged in a minute, preferably about 2% at

the most of the total amount of hydrogen chloride release stoichiometrically in the reaction. This is another way to express the prevention of a quantitatively heavy discharge of hydrogen chloride.

It is, within certain limits, advantageous to minimize the momentary discharge of hydrogen chloride, so that the breaking of the carrier particles would be avoided as efficiently as possible. According to one embodiment of the invention the release of the hydrogen chloride created in the reaction between the carrier particles and the titanium tetrachloride is disributed to a molar velocity that does not exceed the threefold, preferably double, value of the molar mean velocity of the release.

The invention is based on the idea that the reaction between the carrier particles and the TiCl$_4$ is maintained in such a way that a sudden discharge of the hydrogen chloride is prevented during the activation. The attenuation of the sudden discharge i.e. the distribution of the hydrogen chloride release can be carried out by any suitable chemical and/or physical means. The prevention of sudden chemical discharges is in the technical chemistry a general measure and the present invention is not related to certain embodiments of this general measure only, but expressly to the use of this measure to prevent the formation of finely-divided material in a procatalyst.

The release of the hydrogen chloride can be distributed by selecting a correct adding order and adding velocity of the reagents. The adding order preferably is such that the TiCl$_4$ is added to the carrier particles and not vice versa. Moreover, the carrier particles have preferably been suspended into an inert reaction medium. According to one embodiment of the invention TiCl$_4$ is controllably added to a liquid suspension of carrier particles consisting of MgCl$_2$-C$_2$H$_5$OH-complex during 0.5 to 3 hours, preferably

about 1.0 hour. As the medium of liquid suspension in
regard to reagents inert hydrocarbons are usually used,
the amount of which can be regulated so as to decrease the
discharge tendency of the hydrogen chloride.

The controlled, slow adding of $TiCl_4$ reduces the discharge
risk of the hydrogen chloride by producing hydrogen chlo-
ride more slowly (see the reaction formula (1)). Hydrogen
chloride has then time to diffund out from the carrier
particles before oversaturation of hydrogen chloride in
the solution, leading to gas formation in the pores takes
place. Moreover, at least some stages in the reactions
between a $MgCl_2$-C_2H_5OH-complex and $TiCl_4$ apparently are
exothermic, whereby the slow adding of $TiCl_4$ enables a
slow removal of heat from the carrier particles and thus
prevents the carrier particles from heating locally above
the discharge temperature of the hydrogen chloride.

The aforesaid also shows that $TiCl_4$ shall preferably be
added in so low a temperature that no fast reaction nor a
discharge of hydrogen chloride will take place. According
to one embodiment $TiCl_4$ is added at the temperature -30 to
-10°C and preferably at the temperature -25 to -15°C.

Due to the thermodynamic and/or physical balancing systems
in the pores of the carrier particles and the $TiCl_4$-solu-
tion hydrogen chloride is released during a long time
after the adding of the $TiCl_4$. Hereby it is advantageous
to raise the temperature during the adding of the $TiCl_4$
and/or after it with a controlled slow velocity about 5 to
20°C/h, more advantageously with a velocity about 5 to
15°C/h. It is worth continuing this slow increase of the
temperature up to a temperature of +40°C and especially
above it, when the internal donor has been added to the
reaction mixture of the carrier particles and the $TiCl_4$.

The release of the hydrogen chloride created in the reac-

tion can also be distributed by using a strong agitation during the reaction between the carrier particles and the TiCl$_4$. Although the strength of the agitation is dependent of many factors such as other means for distributing the release of the hydrogen chlorid, it can be said that the amount of agitation exceeds in this invention the conventional agitation values and causes an essential distribution of the release of the hydrogen chloride. As in the preparation of procatalyst compositions the agitation has often been accused for the breaking of the carrier particles, it is very surprising that the adding of agitation will help keeping the carrier particles undamaged. The realization to add agitation to reach the aims of this invention must be seen against this background. Be it mentioned that in the reactor used in connection with this invention the starting speed of rotation of the mixer was raised when going over to the method according to this invention from the value 15rpm to the value 30rpm.

Another way to increase the material and heat transfer distributing the release of the hydrogen chloride is to alter the viscosity of the liquid reaction mixture. This can take place, as mentioned above, by selecting a suitable dispersion medium such as C$_5$-C$_8$-hydrocarbon, but it can also take place by adding to the reaction mixture extra liquid reducing the viscosity.

A further way to distribute the release of the hydrogen chloride created in the reaction is to use an overpressure during the reaction. The overpressure has both a thermodynamic and a physical influence on the release of the hydrogen chloride. The thermodynamic influence is based on the prevention of the evaporation of the hydrogen chloride, which reflects back to the distribution reaction optionally creating hydrogen chloride and slowing it down. The physical influence is based on the fact that a higher pressure raises the gasifying temperature of the hydrogen

chloride and prevents the gasification at a certain tempe-
rature. According to one embodiment overpressure is used
during the reaction which is in the order of 1 to 100
bars, preferably about 1 to 50 bars and most preferably 1
to 5 bars.

The release of the hydrogen chloride created in the reac-
tion can also be distributed by leading to the reaction
mixture or above it nitrogen gas. The use of an inert gas
flow influences principally physically so that the hydro-
gen chloride content reduced by the environment accelera-
tes the removal of the hydrogen chloride created in the
reaction from the pores, whereby the saturation point of
the hydrogen chloride corresponding to the gasification
point will never be reached. It is, however, worth while
using the nitrogen or other inert gas carefully for ther-
modynamically its influence is the opposite i.e. by remo-
ving rapidly hydrogen chloride from the pores of the car-
rier particles the possible distribution reaction creating
hydrogen chloride will be accelerated and will produce
abundantly of heat causing discharging of hydrogen chlori-
de.

It is also possible to add to the reaction mixture a li-
quid dissolving the non-gasifying product of the reaction
between the complex particles and the $TiCl_4$. As was pre-
sented above in the reaction formula (1), as a result of
the reaction between a $MgCl_2$-C_2H_5OH-complex and $TiCl_4$ there
is created in addition to the activated magnesium chloride
and hydrogen chloride ethoxytitanium trichloride, the
presence of which in the same solution with hydrogen chlo-
ride decreases the hydrogen chloride absorption capacity
of the solution and thus also the gasification temperature
of the hydrogen chloride. By adding a substance dissolving
ethoxytitanium trichloride the releasing temperature of
the hydrogen chloride can be raised and its release dist-
ributed according to the aim of the invention. The pro-

ducts of the reaction between the complex and $TiCl_4$, such as ethoxytitanium chloride and hydrogen chloride, can also be removed by changing during the reaction the excess amount of $TiCl_4$. As appears from the preliminary tests, the composition of the $MgCl_2$-C_2H_5OH-complex has a decisive effect on how rapidly the hydrogen chloride created in the reaction between the complex and $TiCl_4$ is released. The preliminary results and the reaction formula (1) show that the discharge velocity increases when the C_2H_5OH-content increases. Simultaneously, however, $MgCl_2$'s ability to become activated with $TiCl_4$ also increases, so an optimum must be found for the ethanol content of the complex, which theoretically can vary between 1 and 6, which optimum is dependent on how efficiently the release of the hydrogen chloride created in the reaction can be distributed by other means. According to one embodiment of the invention the molar ratio between the $MgCl_2$ and C_2H_5OH of the $MgCl_2$-C_2H_5OH-complex used as the material of the carrier particles is between 2.5 to 3.5 and preferably between about 2.7 to 3.3. As too large ethanol contents almost always cause hydrogen chloride discharges breaking carrier particles, it can generally be said that the C_2H_5OH-content must be below about 60% of the weight of the procatalyst carrier material.

As the too large carrier particles are broken more easily and due to their deep pore structures accentuate the factors leading to a rapid discharge of the hydrogen chloride, it is advantageous to use carrier particles, the size of which is below about 150μm.

The success of the invention is also influenced by the water content, mechanical strength, particle morphology and particle size distribution of the carrier particles. Therefore it has been noticed that such carrier particles consisting of $MgCl_2$-C_2H_5OH-complex are particularly suitable for the method according to the invention that have

been prepared by a spray-crystallization method. According to one preferred embodiment the complex melt, the composition of which is a $MgCl_2 \cdot 3.5C_2H_5OH$ and the temperature about 120-130°C, is sprayed through a distributing nozzle into a chamber in which the temperature is about 30 to 50°C, after which the stiffly flowing drops are conducted through another zone, the temperature of which is about 10°C lower and where the particles finally solidify. Particles prepared by this kind of a method are mechanically much stronger than e.g. the particles prepared by spray-evaporation and are thus particularly suitable for the method according to the invention, in which the discharge tendency of the hydrogen chloride sets high mechanical requirements for the particles. Simultaneously, particles are created giving a pore volume in the procatalyst, which is suitable for the method according to the invention.

The release of the hydrogen chloride can also be accelerated by the presence of an internal donor in the reaction mixture of carrier particles and $TiCl_4$. This is due to the fact that the reactions of the donor taking place in connection with the adding usually are exothermic. If the donor is added at a stage or in a temperature range where a discharge of the hydrogen chloride is possible, it may, in fact, lead to an uncontrolled release of the hydrogen chloride. This can happen e.g. when the reaction mixture after the adding of the $TiCl_4$ is heated to a temperature of about +20°C and and the donor is added to the reaction mixture. According to one embodiment it is advantageous to distribute the release of the hydrogen chloride created in the reaction in connection with the adding of the internal donor by not adding the donor into the reaction mixture until about 0.5 to 6 hours, preferably about 2 to 5 hours, after the adding of the $TiCl_4$. It is also important to add internal donor into the reaction mixture controllably during about 0.5 to 1.5 hours. To be absolutely sure the heating temperature must not be increased until about 1 to

3 hours after the adding of the donor, whereby the adding of the donor does not cause strong hydrogen chloride discharges.

5   The above-mentioned measures for the distribution of the release of the hydrogen chloride created in the reaction can, according to the invention, be used alone or then combined in any possible way. According to one embodiment of the invention the measures are used in the manner shown
10   in figure 5.

       In figure 5 a temperature profile according to one embodiment of the invention has been presented when procatalyst compositions are prepared with a reaction between $MgCl_2$-
15   C_2H_5OH-complex and $TiCl_4$. In the figure:
       A is a slow increase of temperature after the first adding of $TiCl_4$,
       B is the delay of the reaction after the adding of the donor,
20   C is a more rapid increase of temperature for the completion of the first reaction between the carrier and the $TiCl_4$,
       D is the completion of the first reaction between the carrier and the $TiCl_4$,
25   E is the second treatment of the carrier with $TiCl_4$,
       F is the washing and
       G is the drying.

       According to the invention it is advantageous to carry out
30   one or several of the above-mentioned measures for the distribution of the release of the hydrogen chloride created in the reaction in the points I, II, and III marked in the figure. Hereby, it is natural to carry out the measures connected with the adding of the $TiCl_4$ and the heating
35   taking place in connection with it in point I and the corresponding measures connected with the adding of the donor in points II and III. In other respects the measures

can be optimized, taking into consideration the whole pro-
cess, for each reactor and the desired product.

As even the smallest impurity can disturb the reaction and
cause a surprising hydrogen chloride discharge, the subs-
tances must be as pure as possible and above all dry.
Special attention must be paid to the medium and to the
inert gas, so that no harmful sidereactions can occur. To
keep the reaction environment as clean as possible it is
advantageous to use a multi-function reactor, by which the
activation, washing and drying stages can be carried out
without removing the procatalyst or its intermediary pro-
duct from the reactor. This kind of a reactor and method
have been presented in the Finnish Patent No. 83329, which
is hereby attached to the application as a reference.

In the following a few comparative examples and embodi-
ments are presented for illustrating the invention.

Starting materials

The $TiCl_4$ used in the synthesis was liquid and non-aque-
ous.

The $MgCl_2$-C_2H_5OH-complex carrier was prepared from complex
melt, to the composition of which $MgCl_2 \cdot 3.5C_2H_5OH$ was ad-
justed. Melt was sprayed at the temperature of about 120
to 130°C through a nozzle structure distributing it, the
temperature of the reception zone of which was about 30 to
50°C. From the reception zone the melt drops were conduct-
ed through a slightly colder zone for the final hardening
of the particles. Moreover, the the particles were sieved
so as to have the particle size below about 150µm. The
composition of the final particles was about $MgCl_2 \cdot 3C_2H_5OH$.

The morphology of the carrier particles was splendid. The

particle size distribution was between 1.50 to 3.4 (span) and the particles did not contain finely-divided material. The microscope pictures of the carrier particles have been presented in connection with the microscope pictures of
5 the procatalysts and the polymers in the handling of the results.

Comparative example 1

10 A multi-function reactor furnished with a sieve bottom, the volume of which was $1.5m^3$, was cooled to the temperature of -20°C. Then the inert hydrogen carbon solvent (Neste product LIAV), $TiCl_4$ and the carrier, $MgCl_2 \cdot 2.7C_2H_5OH$, were added into the reactor, in the order
15 mentioned. The amount of the carrier was 44kg and the ratio $TiCl_4$ (mole)/carrier C_2H_5OH (mole) was 10. The ratio LIAV (kg)/carrier (kg) was 4.5 and the ratio $TiCl_4$ (mole)/Mg (mole) was 30. The agitation velocity was 15rpm.

20 After the adding of the reagent the temperature was slowly with the velocity of 0.22°C/min. raised to the temperature +20°C. The agitation velocity still was 15rpm.

Five hours after the adding of the reagent di-isobutylph-
25 thalate(DIBP)-donor was added at the temperature +20°C so that the ratio donor (mole)/Mg (mole) was 0.15. Then the temperature was raised with the mean velocity of about 0.1°C/min. to the value 110°C. The agitation velocity still was 15rpm. The temperature and the agitation were
30 maintained for about 1 hour, after which the activation residues with the excess amount of $TiCl_4$ were removed by rinsing through the sieve bottom of the reactor.

The second treatment with $TiCl_4$ was carried out by adding
35 the reagent into a purified solid intermediary product. The temperature still was 110°C, the agitation velocity 15rpm and the reaction time 2 hours. The ratio $TiCl_4$ (mo-

le)/Mg (mole) being also now 30.

Finally, the product was washed four times with a hydrogen
carbon solvent (LIAV) so that the ratio LIAV (kg)/carrier
5   (kg) was 9. During the washing the agitation velocity was
about the same as above. After this the product was dried
with a N_2-gas flow at the temperature 70°C without agita-
tion.

10   In connection with this comparative example it was noticed
that when carrier was added above the $TiCl_4$ the mixture
began to boil already at the temperature of -20°C. The
particle size distribution of the catalyst product was
such that 64.7% by weight of it had the diameter below
15   20μm. D_{50} was 17μm and the width of the particle size
distribution i.e. the span figure was 3.1. The portion of
the finely-divided material in the polymer produced with
the catalyst was 70% by weight (d<1mm) and the bulk densi-
ty was 0.43g/ml.
20

Comparative examples 2 to 5

A multi-function reactor furnished with a sieve bottom,
the volume of which was 1.5m³, was cooled to the tempera-
25   ture of -20°C. Then the inert hydrogen carbon solvent
(Neste product LIAV), 24kg of the carrier, $MgCl_2 \cdot 3.0C_2H_5OH$
and $TiCl_4$ were added into the reactor, in the order men-
tioned. The ratio $TiCl_4$ (mole)/carrier C_2H_5OH (mole) was
10, the ratio LIAV (kg)/carrier (kg) was between 4.5 to 9
30   and the ratio $TiCl_4$ (mole)/Mg (mole) was 30. The agitation
velocity was 15rpm.

After the adding of the reagent the temperature was slowly
with the velocity of 0.22°C/min. raised to the temperature
35   +20°C. The agitation velocity still was 15rpm. 3 to 5
hours after the adding of the reagent di-isobutylphthala-
te(DIBP)-donor was added at the temperature +20°C so that

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the ratio donor (mole)/Mg (mole) was 0.15.

Then the temperature was raised with the mean velocity of
about 1°C/min. to the value 110°C. The agitation velocity
5   still was 15rpm. The temperature and the agitation were
maintained in about 1 hour, after which the activation
residues with the TiCl$_4$ excess amounts were removed by
rinsing through the sieve bottom of the reactor.

10   The other treatment with TiCl$_4$ was carried out by adding
the reagent into a purified solid intermediary product.
The temperature still was 110°C, the agitation velocity
15rpm and the reaction time about two hours. The ratio
TiCl$_4$ (mole)/Mg (mole) also now 30.

15
Finally, the product was washed four times with a hydrogen
carbon solvent (LIAV) so that the ratio LIAV (kg)/carrier
(kg) was 9. During the washing the agitation velocity was
about the same as above. After this the product was dried
20   with a N$_2$-gas flow at the temperature 70°C without agita-
tion.

In connection with these comparative examples it was noti-
ced that during the heating gas was produced. The particle
25   size distribution of the catalyst product was such that 11
to 28% by weight of it had the diameter below 20μm. D$_{50}$
was between 30 and 62μm and the width of the particle size
distribution i.e. the span figure was between 1.46 and
2.96. The rest of the properties are presented in connec-
30   tion with the results.

Comparative examples 1 to 4

A multi-function reactor furnished with a sieve bottom,
35   the volume of which was 1.5m^3, was cooled to the tempera-
ture of -20°C. Then the inert hydrogen carbon solvent
(Neste product LIAV), carrier, MgCl$_2$·3.0C$_2$H$_5$OH, and TiCl$_4$

were added into the reactor, in the order mentioned. The
amount of the carrier varied between 24 to 29kg and the
ratio $TiCl_4$ (mole)/carrier C_2H_5OH (mole) was 10. The ratio
LIAV (kg)/carrier (kg) was 9.0 and the ratio $TiCl_4$ (mo-

5   le)/Mg (mole) was 30.

Deviating from the comparative example the starting velo-
city of the agitation was 30rpm, the overpressure of the
reactor was 22.5 bars and through the reactor was conduct-

10   ed dry N_2-gas with the flowing velocity of 5kg/hour until
the maximum temperature was reached.

After the adding of the reagents the temperature was slow-
ly raised with the velocity of 0.22°C/min. to the tempera-

15   ture +20°C. At this stage the agitation had been reduced
from the original value of 30rpm to the usual value of
15rpm in order to decrease the mechanical strain caused by
the agitation.

20   Three hours after the adding of the reagents di-isobu-
tylphthalate(DIBP)-donor was added at the temperature of
+20°C so that the ratio donor (mole)/Mg (mole) was 0.15.

Then the temperature was raised with the mean velocity of

25   about 1°C/min. to the value 110°C, whereby the overpressu-
re and the N_2-flow were removed. The agitation velocity
still was 15rpm. The temperature and the agitation were
maintained in about 1 hour, after which the activation
residues with the $TiCl_4$ excess amounts were removed by

30   rinsing through the sieve bottom of the reactor.

The other treatment with $TiCl_4$ was carried out by adding
the reagent into a purified solid intermediary product.
The temperature still was 110°C, the agitation velocity

35   15rpm and the reaction time about two hours. The ratio
$TiCl_4$ (mole)/Mg (mole) was also now 30.

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Finally, the product was washed three times with a hydrogen carbon solvent (LIAV) so that the ratio LIAV (kg)/carrier (kg) was 9. During the washing the agitation velocity was about the same as above. After this the product was dried with a N_2-gas flow at the temperature 70°C without agitation.

In connection with these comparative examples no boiling was noticed during the heating. The particle size distribution of the catalysts was such that 21 to 22% by weight of it had the diameter below 20μm. D_{50} was 44 to 62μm and the width of the particle size distribution i.e. the span figure was 2.25 to 2.59 (except in the fourth pilot-test). The rest of the properties are presented in connection with the handling of the results.

Test polymerization

All the procatalysts of the comparative examples and the embodiments prepared in laboratory or pilot-scale were tested under standard polymerization conditions. A 2-liter bench reactor was used. 20 to 30mg of procatalyst was used in each test polymerization run. To this amount 620μml of triethyl aluminium co-catalyst and 200μml of 25% heptane solution of an internal cyklohexylmethyl methoxysilane donor were added. As the intermediary medium 900ml of heptane was used. The polymerizations were carried out at the temperature of +70°C and in the propene monomer pressure of 10 bars. The partial pressure of hydrogen during the polymerization was 0.2 bars. 11mmol H_2 was added to adjust the molecular weight. The polymerization was continued for three hours. Thereafter the activity of the procatalyst was measured on the basis of the polymerization yield. The solvent portion of the polymer was measured by dissolving a certain polymer amount into the solvent and measuring the evaporation residue of the pure solution.

The bulk density and the particle size distribution of all
the polymer samples were determined. In connection with
the particle size distribution measurements the total
amount of the finely-divided material was estimated. Here-
5   by all polymer particles, the diameter of which was smal-
ler than 1mm was defined as finely-divided material. The
isotacticity was measured by means of heptane elution and
the isotacticity index was measured by using the results
of the evaporation residue measurements. The melt index
10   was measured at the temperature of 230°C by using a 2.16kg
weight.

Results

15   The above-mentioned test runs have been carried out in
pilot-scale. The original tests were carried out in labo-
ratory. Hereby, it was observed that in pilot-scale there
occurred problems that did not occur in laboratory scale.
In laboratory tests the release of the hydrogen chloride
20   gas was uniform in all the tests, whereas in the pilot-
scale in the comparative tests a heavy discharge of hydro-
gen chloride gas took place as a difference from the embo-
diment tests, in which the release of the hydrogen chlori-
de could be distributed by the measures according to the
25   invention.

The release of hydrogen chloride was followed in the embo-
diments by registering how much the exhaust of the reactor
could open the escape valve connected with the reactor and
30   regulating the pressure of the reactor. In figure 6 the
opening of this kind of a valve is presented as a function
of the temperature and the time. Higher up in the figure
there is presented the gradient of the temperature of the
reactor i.e. the profile and lower down the opening of the
35   valve i.e. the escaping velocity of the hydrogen chloride
gas as a function of the time. The escaping velocity of
the hydrogen chloride is relatively even and does not show

any peaks like those shown in figure 3 during the heating.

The titanium content, the donor content, the particle size
distribution, the catalyst yield, the catalyst activity,
the polymer-isotacticity, the polymer melt index and the
polymer-bulk density of the procatalysts of the embodi-
ments prepared in laboratory and in pilot-scale were nor-
mal for catalysts of corresponding type.

The titanium content varied between 2.4 and 3.6% by weight
in laboratory catalysts and between 2.4 and 4.5% by weight
in pilot-procatalysts. The donor content varied between
15.9 and 19.2% by weight in laboratory-procatalysts and
between 9.7 and 15.4% by weight in pilot-procatalysts (in
embodiment 1 the pilot-scale donor feed was unsuccessful).

The particle size distribution of the procatalysts appear
from table 1. Only in the last i.e. fourth pilot-scale
preparation a small procatalyst decomposition could be
noticed, which can be seen as a broad distribution, the
span-figure of which was 3.41.

The procatalyst yield was satisfactory varying between 74
and 99% in pilot-run and between 82 and 92% in laboratory.
This shows that finely-divided material has not e.g. been
rinsed off to any in any greater extent in the pilot-run
compared to the laboratory-run.

The activity of the pilot-procatalysts was at its best
15.8kgPP/g cat, which is a good value and of the same
order as in the procatalysts prepared in laboratories.

The polymer-isotacticity varied in laboratory-procatalysts
between 98.9 and 99.3% (the index between 98.3 to 98.9)
and in the pilot-procatalysts between 96.8 and 97.5% (the
index between 93.3 and 98.1) being at a satisfactory le-

vel.

The polymer melt indices varied in laboratory procatalysts between 4.3 and 9.6 and in pilot-procatalysts between 5.0 and 7.4 (the MI of the fourth run was exceptionally 19.4) corresponding the melt index of a normal polypropene.

The polymer bulk densities varied in laboratory procatalysts between 0.41 and 0.47g/ml and in pilot-procatalysts between 0.40 and 0.44g/ml.

Special attention was paid to the particle size distribution of the polymer material given by the procatalysts prepared by the method according to the invention. The results have been presented in table 2. A graphical presentation can be found in figure 7.

In table 2 (see page 20) only the particle size distribution of the polymers obtained with the laboratory- and pilot-procatalysts according to the embodiments 1 to 4, whereas in figure 8 polymers prepared with the laboratory- and pilot-procatalysts according to the comparative examples and the polymers prepared with the laboratory- and pilot-procatalysts according to the embodiments have been compared. The figure clearly shows that the comparative examples and the embodiments give the same kind of results when a procatalyst synthesis carried out in laboratory scale is concerned.

When going over to pilot-scale a remarkable improvement can be achieved with the measures according to the invention compared with the procatalysts according to the comparative examples. In pilot-scale the portion of the finely-divided material of the polymer can be reduced to at least about the fourth and at the utmost to even less than a tenth of the results of the comparative tests. In the pilot comparative example 1, where the adding order of the

reagents was different (see the directions above) as much as 70% by weight was obtained as the portion of the finely-divided substance, which value is much higher than

5   those of the pilot embodiments.

In figures 9 to 12 electron microscope pictures of the carrier of the embodiment 1 (fig. 8), the laboratory-procatalyst (fig. 9), the pilot-procatalyst (fig. 10), the

10 polymer obtained with a laboratory-procatalyst (fig. 11) and the polymer obtained with a pilot procatalyst (fig. 12) are shown. These figures relating to the embodiment 1 do visually represent well the morphology of the product, proceeding from a spray-crystallized carrier to a finished

15 polypropene product. When figures 8, 10 and 12 are compared, it can be seen that the portion of the finely-divided material in the polymer or the procatalyst is not much higher than in the carrier. When figures 10 and 12 are compared with figures 9 and 11 it can be seen that both

20 the procatalyst and the polymer are a little more agglomerated in the pilot-scale synthesis than in the laboratory-scale synthesis. This tendency was not, however, as strong as in the embodiments 2 to 4.

Table 1   The particle size distribution of the procata-
lysts prepared in pilot- and laboratory-scale

Embodiment	D(0.1) μm	D(0.5) μm	D(0.9) μm	Span
Pilot 1	8.4	44.3	108.1	2.25
2	6.7	52.4	142.3	2.59
3	11.8	80.4	108.6	2.17
4	7.5	38.7	139.5	3.41
Laboratory 1	6.1	36.8	106.9	2.75
2	10.7	63.8	203.6	3.02
3	7.4	44.0	107.2	2.27
4	6.3	51.1	119.8	2.22

Table 2   Polymer particle size distributions given by the
catalysts in pilot- and laboratory-scale

Embodiment	Procatalyst	2.0 mm	1.0 mm	0.5 mm	0.18 mm	0.1 mm
1	Pilot	45.0	45.6	8.9	0.5	0.0
	Lab.	67.9	30.1	1.5	0.3	0.1
2	Pilot	47.1	46.8	4.5	0.9	0.4
	Lab.	65.0	31.5	3.4	0.3	0.0
3	Pilot	61.2	29.7	7.2	1.6	0.3
	Lab.	64.4	31.1	3.6	0.7	0.2
4	Pilot	50.6	41.3	7.1	0.9	0.1
	Lab.	38.6	48.7	10.6	1.5	0.5

In the enclosed figures 1 to 12 the following is present-
ed:

Fig. 1: Formation of the finely-divided substance in PP-
polymer when comparing pilot-catalyst to laboratory cata-
lyst,

Fig. 2: Correlation between the amount of the finely-di-
vided fraction of the polymer and the maximum releasing
velocity (ml/min) of the HCl created in the catalyst syn-
thesis,

Fig. 3: Release of HCl when heating a system containing a
$MgCl_2$-C_2H_5OH-complex, HCl and $TiCl_4$,

Fig. 4: The rate of HCl gas release as a function of the
temperature, when the system contains a $MgCl_2$-C_2H_5OH-comp-
lex, $TiCl_4$, and HCl,

Fig. 5: A preferred use of the measures according to the
invention in a procatalyst process; (A) slow increase of
temperature after a $TiCl_4$-addition, (B) delay of the reac-
tion during the adding of the donor and after it, (C)
increase of temperature for the completion of the reacti-
on, (D) first titanization, (E) second titanization, (F)
washing, (G) drying,

Fig. 6: Releasing velocity of the hydrogen chloride (lower
curve) as a function of the temperature (upper curve) and
time,

Fig. 7: Total amount of finely-divided substance (d<1 mm)
in polymers prepared with laboratory- and pilot-catalysts
of the comparative examples (old) and the embodiments,

Fig. 8: carrier of embodiment 1, length unit 100µm,

Fig. 9: laboratory procatalyst of embodiment 1
(25µm),

5

Fig. 10: pilot procatalyst of embodiment 1 (25µm),

Fig. 11: polymer obtained with laboratory procatalyst of
embodiment 1,

10

Fig. 12: polymer obtained with pilot procatalyst of embo-
diment 1.

Claims

1.   Method for the preparation of a particulate pro-catalyst composition intended for the polymerization of olefins by reacting the carrier particles consisting of a $MgCl_2$-C_2H_5OH-complex with $TiCl_4$, whereby hydrogen chloride is formed, **characterized** in that the carrier particles are maintained undamaged during the reaction by distributing the release in the reaction or from the reaction of the hydrogen chloride created in the reaction to a molar velocity not exceeding the fivefold value of the molar mean velocity of the release.

2.   Method according to claim 1, **characterized** in that the release of the hydrogen chloride created in the reaction is distributed to a volume velocity not exceeding the threefold, preferably double, value of the mean volume velocity of the release.

3.   Method according to claim 1 or 2, **characterized** in that the release of the hydrogen chloride from the carrier complex or the reaction mixture is restricted so that not more than about 5%, preferably less than about 2%, is discharged in a minute from the stoichiometrically released hydrogen chloride.

4.   Method according to claim 1, 2, or 3, **characteri-**zed in that the release of the hydrogen chloride is dis-tributed by controllably adding $TiCl_4$ into the liquid sus-pension of the carrier particles during 0.5 to 3.0 hours, preferably during 1.0 hour.

5.   Method according to claim 4, **characterized** in that the $TiCl_4$ is added at the temperature of -30...-10°C, preferably at the temperature of -25...-15°C.

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6.   Method according to claim 5, **characterized** in
that the temperature is raised during the adding of the
TiCl₄ or after it at the velocity of about 5-20°C/h, pre-
ferably at the velocity of about 10°C/h, between about
-20...+40°C.

7.   Method according to any of the preceding claims,
characterized in that the release of the hydrogen chloride
created in the reaction is distributed by using strong
agitation during the reaction.

8.   Method according to any of the preceding claims,
characterized in that the release of the created hydrogen
chloride is distributed by using in the reaction mixture a
liquid reducing its viscosity.

9.   Method according to any of the preceding claims,
characterized in that the release of the hydrogen chloride
created in the reaction is distributed by using during the
reaction an overpressure, which preferably is of the order
of 1 to 100 bars, more preferably about 1 to 50 bars, and
most preferably abnout 1 to 5 bars.

10.   Method according to any of the preceding claims,
characterized in that the release of the hydrogen chloride
created in the reaction is distributed by conducting to
the reaction mixture or above it nitrogen gas.

11.   Method according to any of the preceding claims,
characterized in that the release of the hydrogen chloride
created in the reaction is distributed by using in the
reaction mixture a liquid dissolving the product of a
reaction between TiCl₄ and a MgCl₂-C₂H₅OH-complex.

12.   Method according to claim 11, **characterized** in
that the liquid dissolving the product of a reaction bet-
ween TiCl₄ and a MgCl₂-C₂H₅OH-complex is an excess amount

of TiCl₄ and that TiCl₄ is exchanged during the reaction to new TiCl₄ for the removal of HCl as dissolved in it.

13. Method according to any of the preceding claims, characterized in that a MgCl₂-C₂H₅OH-complex is used, the molar ratio of which between MgCl₂ and C₂H₅OH being 2.5 to 3.5, preferably 2.7 to 3.3.

14. Method according to any of the preceding claims 3 to 13, characterized in that a MgCl₂-C₂H₅OH-complex is used, the C₂H₅OH-content of which is below 60% by weight.

15. Method according to any of the preceding claims, characterized in that carrier particles are used, the size of which is below about 150μm.

16. Method according to any of the preceding claims, characterized in that the carrier particles consisting of MgCl₂-C₂H₅OH-complex have been prepared by spray-crystallization.

17. Method according to any of the preceding claims, characterized in that the release of the hydrogen chloride created in the reaction is distributed in connection with the adding of an internal donor by not adding the donor into the reaction mixture until about 0.5 to 6 hours, preferably about 2 to 5 hours, after the adding of the TiCl₄.

18. Method according to claim 15, characterized in that the internal donor is controllably added into the reaction mixture during about 0.5 to 1.5 hours.

19. Method according to claim 15 or 16, characterized in that heating velocity is not raised until about 1 to 3 hours after the adding of the donor and the raising of the temperature is stopped at about 110 to 120°C.

20. Method according to any of the preceding claims, **characterized** in that essentially the following temperature profile is used:

in which A is a slow increase of the temperature after the first $TiCl_4$-addition,

B is a delay of the reaction after the adding of the donor,

C is a more rapid increase of temperature for the completion of the first reaction between the carrier and the $TiCl_4$,

D is the completion of the first reaction between the carrier and the $TiCl_4$,

E is the second treatment of the carrier with $TiCl_4$,

F is the washing and

G is the drying,

whereby the measures mentioned in the foregoing claims for the distribution of the release of the hydrogen chloride created in the reaction are carried out in points I, II, and III.

21. Method according to claim 18, **characterized** in that the measure according to claims 3, 4, and/or 5 is carried out in point I, and the measure according to

claims 15, 16, and/or 17 is carried out in points II and III.

22.   Method according to any of the preceding claims, characterized in that a multi-function reactor furnished with a sieve bottom is used, by which the activation, washing and drying stages can be carried out without removing the procatalyst or the intermediary product leading to it from the reactor.

AMENDED CLAIMS
[received by the International Bureau on 27 April 1993 (27.04.93);
original claims 1,4 and 11 replaced by amended claim 1; claims 2,3 and 12 - 22
renumbered as claims 3,4 and 9-19; claims 4-7 amended and renumbered 5-8
other claims unchanged (5 pages)]

1.   Method for the preparation of a particulate pro-
catalyst composition intended for the polymerization of
olefins by reacting carrier particles consisting of a
$MgCl_2$-C_2H_5OH-complex with $TiCl_4$, whereby hydrogen chloride
is formed, **characterized** in that one or several steps are
used, in which:

(a) the $TiCl_4$ is controllably added to a liquid suspension
of the carrier particles during 0.5 - 3.0 hours;

(b) the $TiCl_4$ is added at the temperature of -30...-10°C;

(c) the temperature is raised during and after the adding
of the $TiCl_4$ at a rate of about 5...20°C/h to a range of
about -20...+40°C;

(d) vigorous stirring is used during the reaction;

(e) a viscosity lowering liquid is used in the reaction
composition;

(f) over-pressure being of the order of 1...100 bars is
used during the reaction;

g) nitrogen gas is conducted into the reaction composition
or above it, and

(h) liquid dissolving the product formed in the reaction
between the carrier particles and the $TiCl_4$ is used in the
reaction composition,
so that the release of hydrogen chloride per minute is
restricted to not more than 5% of the total hydrogen chlo-
ride amount formed in the reaction in order to maintain
the carrier particles undamaged.

2.   Method according to claim 1, **characterized** in
that the release of the hydrogen chloride created in the
reaction or from the reaction is levelled to a molar velo-
city not exceeding the fivefold value of the mean volume
velocity of the release.

3.   Method according to claim 1 or 2, **characterized**
in that the release of the hydrogen chloride created in
the reaction is levelled to a volume velocity not excee-
ding the threefold, preferably double, value of the mean
volume velocity of the release.

4.   Method according to claim 1, 2, or 3, characteri-
zed in that the release of the hydrogen chloride from the
carrier complex or the reaction mixture is restricted so
that not more than about 2% is discharged per minute from
the total hydrogen chloride amount formed in the reaction.

5.   Method according to claim 1, 2, 3, or 4, charac-
terized in that the release of the hydrogen chloride is
distributed by controllably adding $TiCl_4$ into the liquid
suspension of the carrier particles during about 1 hour.

6.   Method according to any of the preceding claims,
characterized in that the $TiCl_4$ is added at the temperatu-
re of 25...-15°C.

7.   Method according to any of the preceding claims,
characterized in that the temperature is raised during the
adding of the $TiCl_4$ or after it at the velocity of about
5-15°C/h between about -20...+40°C.

8.   Method according to any of the preceding claims,
characterized in that the release of the hydrogen chloride
formed in the reaction is levelled by using during the
reaction an overpressure, which preferably is of the order
of 1 to 50 bars, preferably about 1 to 5 bars.

9.   Method according to claim 8, characterized in
that the liquid dissolving the product of a reaction bet-
ween $TiCl_4$ and a $MgCl_2$-C_2H_5OH-complex is an excess amount
of $TiCl_4$ and that for the removal of HCl dissolved in it
the $TiCl_4$ is exchanged during the reaction to new $TiCl_4$.

10.   Method according to any of the preceding claims,
characterized in that a $MgCl_2$-C_2H_5OH-complex is used, the
molar ratio of which between $MgCl_2$ and C_2H_5OH being 2.5 to
3.5, preferably 2.7 to 3.3.

11.   Method according to any of the preceding claims,
characterized in that a $MgCl_2$-C_2H_5OH-complex is used, the

C_2H_5OH-content of which is below 60% by weight.

12.   Method according to any of the preceding claims, characterized in that carrier particles are used, the size of which is below about 150 μm.
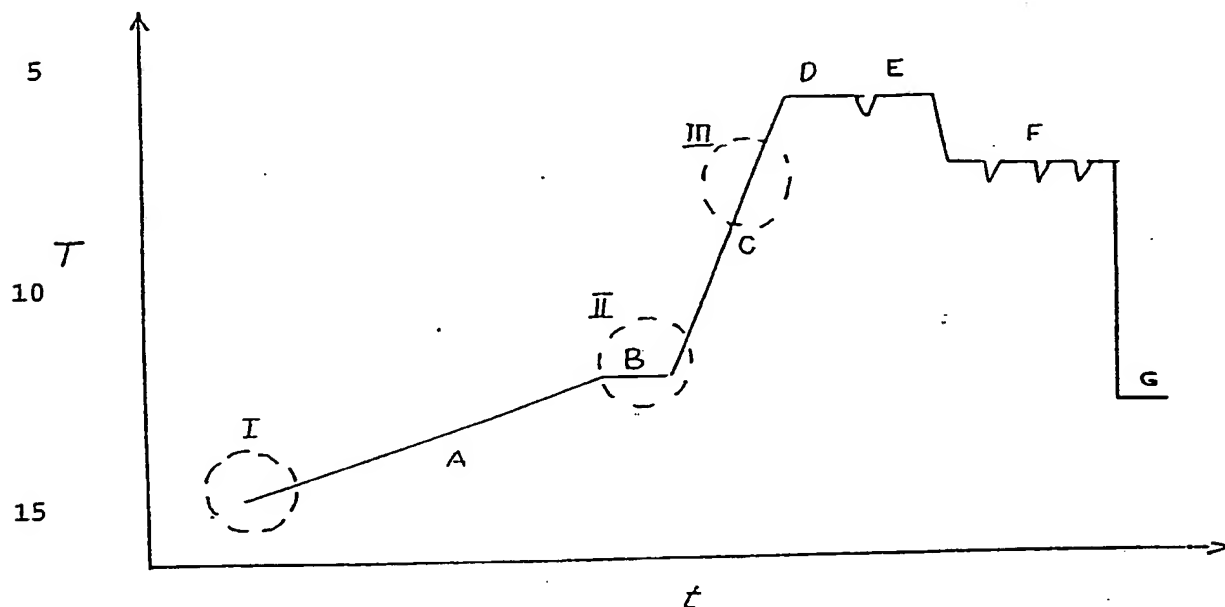
13.   Method according to any of the preceding claims, characterized in that the carrier particles consisting of $MgCl_2$-C_2H_5OH-complex have been prepared by spray-crystallization.

14.   Method according to any of the preceding claims, characterized in that the release of the hydrogen chloride created in the reaction is levelled in connection with the adding of an internal donor by not adding the donor into the reaction mixture until about 0.5 to 6 hours, preferably about 2 to 5 hours, after the adding of the $TiCl_4$.

15.   Method according to claim 12, characterized in that the internal donor is controllably added into the reaction mixture during about 0.5 to 1.5 hours.

16.   Method according to claim 12 or 13, characterized in that heating velocity is not raised until about 1 to 3 hours after the adding of the donor and the raising of the temperature is stopped at about 110 to 120°C.

17.   Method according to any of the preceding claims, **characterized** in that essentially the following temperature profile is used:

in which A is a slow increase of the temperature after the first TiCl$_4$-addition,

B is a delay of the reaction after the adding of the donor,

C is a more rapid increase of temperature for the completion of the first reaction between the carrier and the TiCl$_4$,

D is the completion of the first reaction between the carrier and the TiCl$_4$,

E is the second treatment of the carrier with TiCl$_4$,

F is the washing and

G is the drying,

whereby the measures mentioned in the foregoing claims for the distribution of the release of the hydrogen chloride created in the reaction are carried out in points I, II, and III.

18.   Method according to claim 17, **characterized in** that the measure according to claims 1a), 1b), 1c), 5, 6, and/or 7 is carried out in point I, and the measure accor-

ding to claims 14, 15, and/or 16 is carried out in points II and III.

19.   Method according to any of the preceding claims, characterized in that a multi-function reactor furnished with a sieve bottom is used, by which the activation, washing and drying stages can be carried out without removing the procatalyst or the intermediary product leading to it from the reactor.
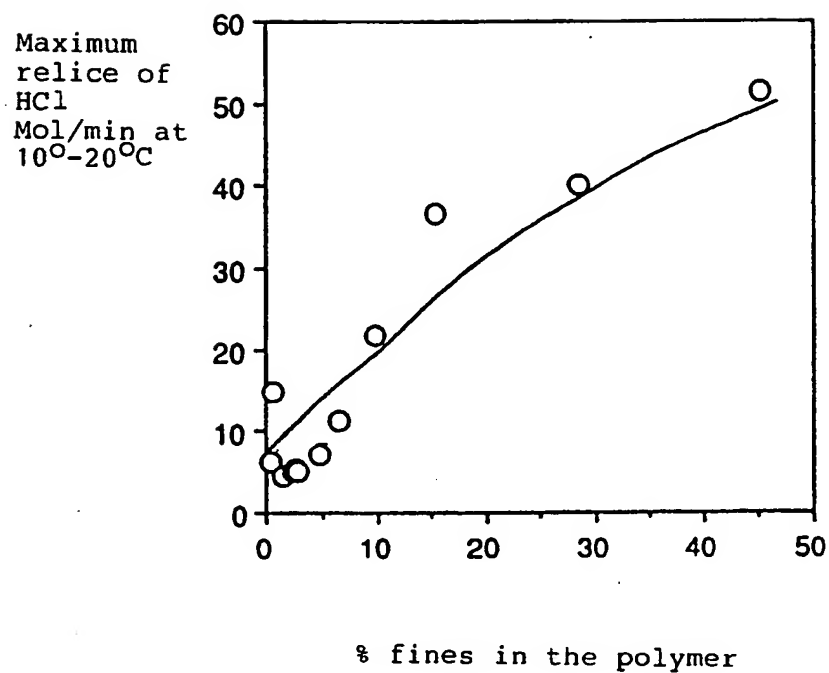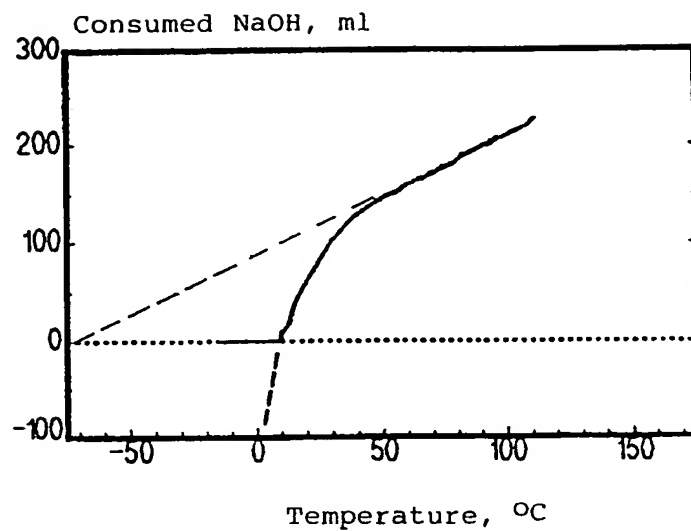
FIG. 1

% fines in the polymer

FIG. 2

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FIG. 3

FIG. 4
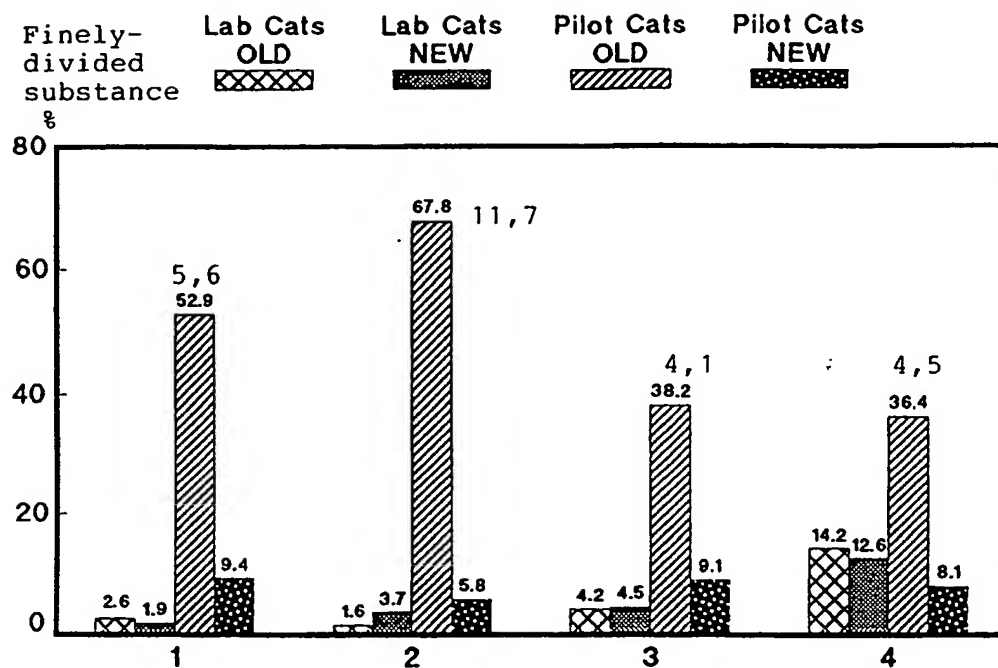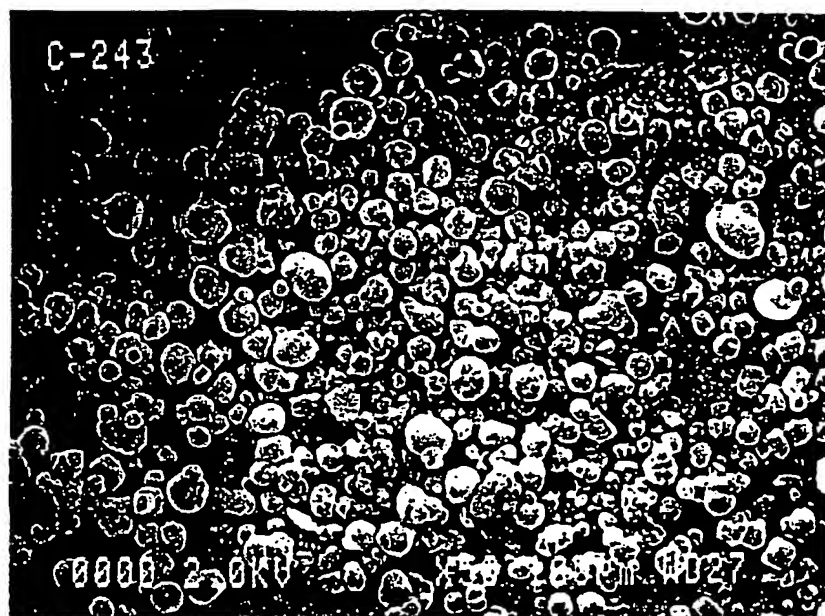
Reaction
temperature

Process time
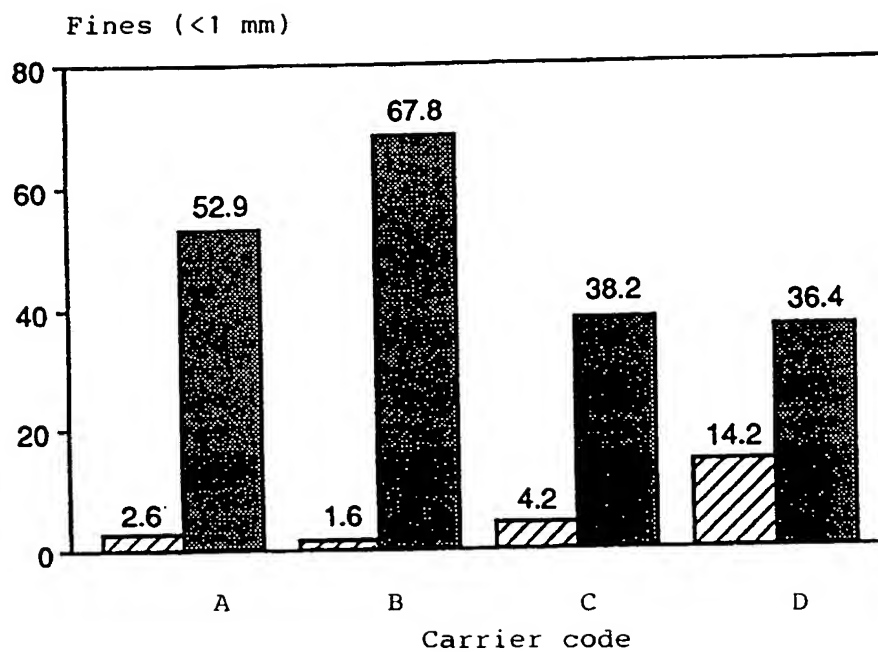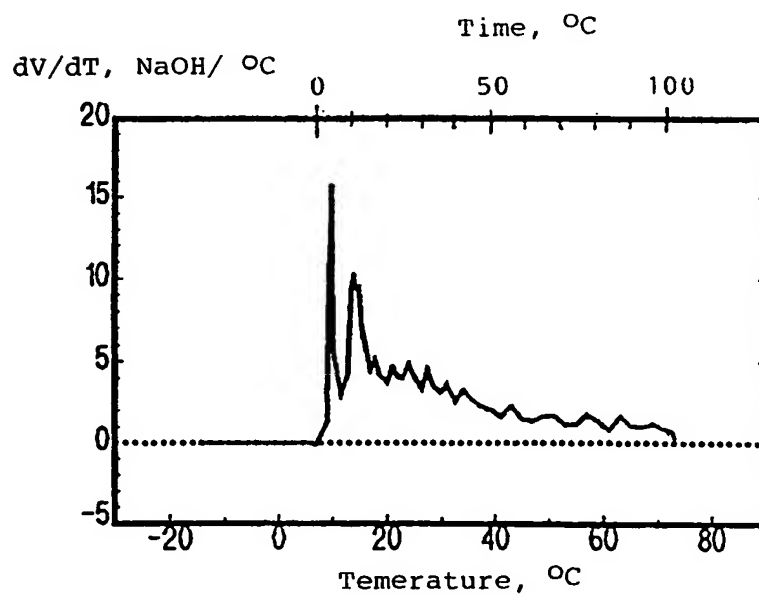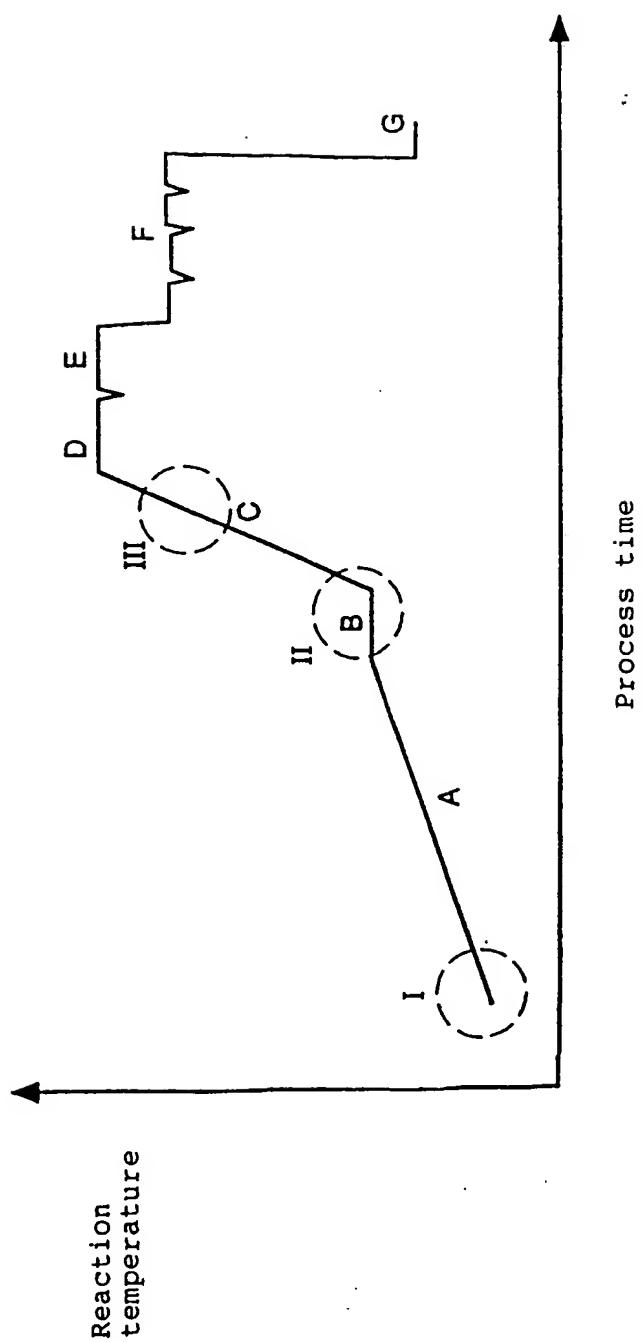
FIG. 5
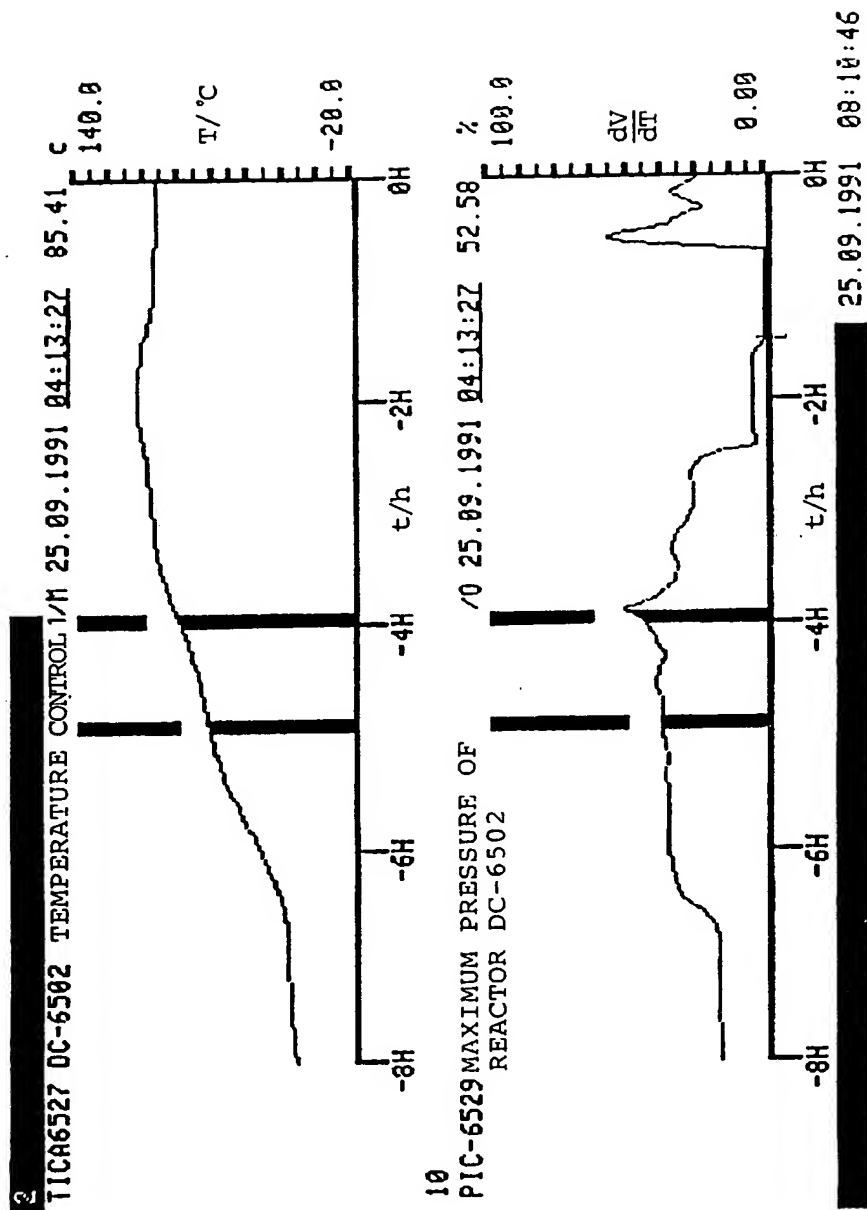
FIG. 6

FIG. 7

FIG. 8   **SUBSTITUTE SHEET**

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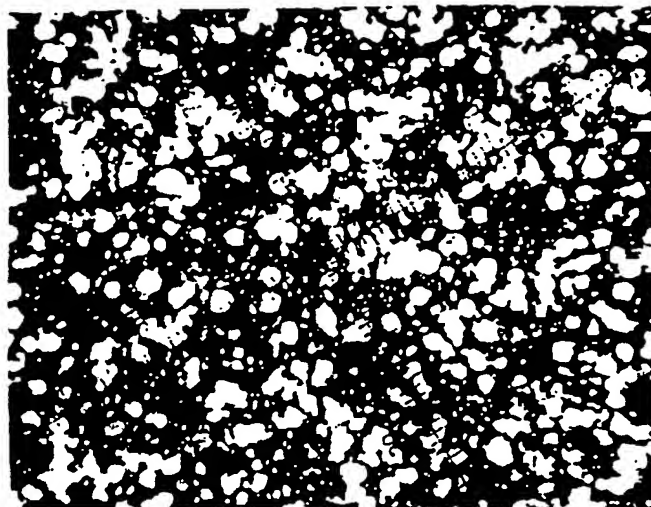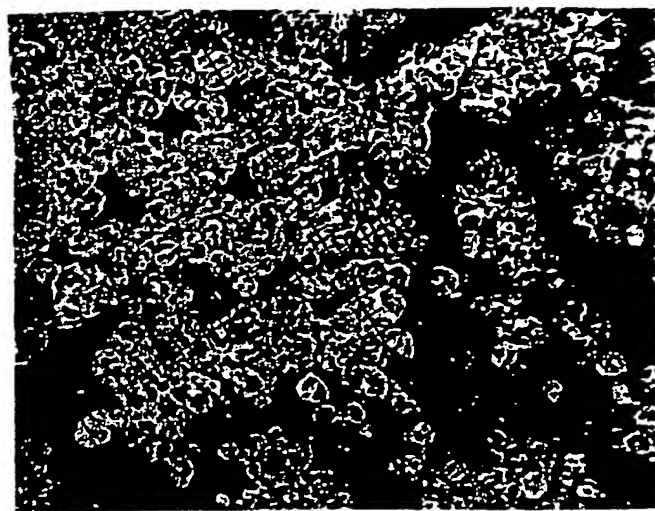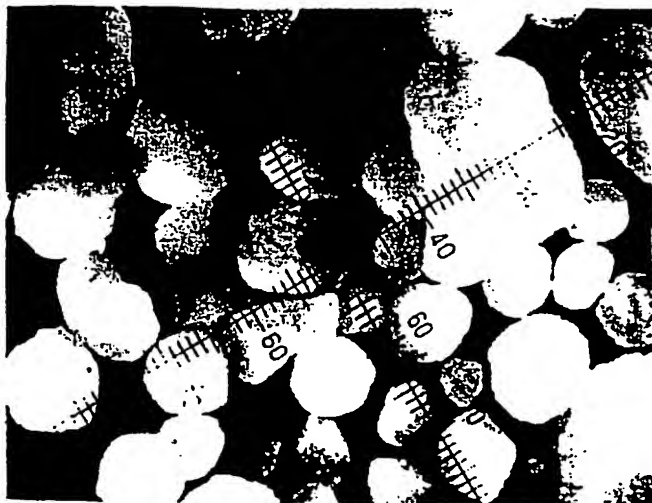

FIG. 9
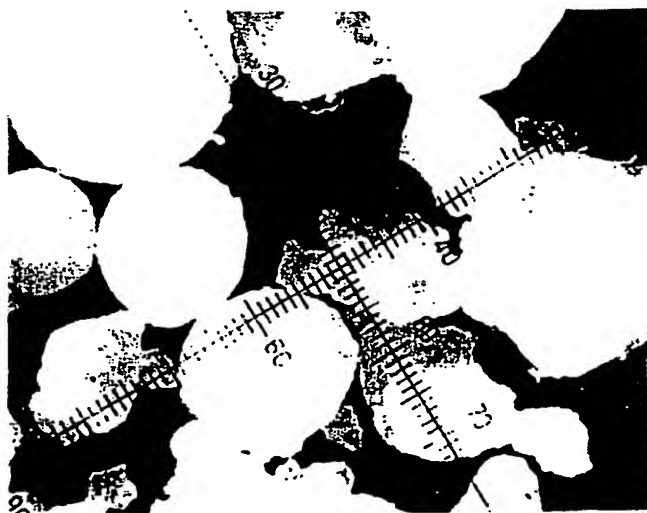

FIG. 10

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FIG. 11

FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 92/00322

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08F 4/02, C08F 4/654

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2, 0424049 (NESTE OY), 24 April 1991 (24.04.91), examples 1 and 4	1-22
	--	
A	WO, A1, 8707620 (NESTE OY), 17 December 1987 (17.12.87)	1
	--	

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" erlier document but published on or after the international filing date	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 March 1993	09 -03- 1993

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Form PCT/ISA/210 (second sheet) (July 1992)

		International application No.
29/01/93		PCT/FI 92/00322

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0424049	24/04/91	JP-A- 3151037	27/06/91
WO-A1- 8707620	17/12/87	CH-A,B- 671767	29/09/89
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		EP-A- 0279818	31/08/88